

# Atomic layer deposition

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**Atomic layer deposition (ALD)** is a thin film deposition technique that is based on the sequential use of a gas phase chemical process. The majority of ALD reactions use two chemicals, typically called precursors. These precursors react with a surface one-at-a-time in a sequential manner. By exposing the precursors to the growth surface repeatedly, a thin film is deposited.<sup>[1]</sup>

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## Introduction

ALD is a self-limiting (the amount of film material deposited in each reaction cycle is constant), sequential surface chemistry that deposits conformal thin-films of materials onto substrates of varying compositions. ALD is similar in chemistry to chemical vapor deposition (CVD), except that the ALD reaction breaks the CVD reaction into two half-reactions, keeping the precursor materials separate during the reaction. Due to the characteristics of self-limiting and surface reactions, ALD film growth makes atomic scale deposition control possible. By keeping the precursors separate throughout the coating process, atomic layer control of film growth can be obtained as fine as  $\sim 0.1 \text{ \AA}$  (10 pm) per monolayer. Separation of the precursors is accomplished by pulsing a purge gas (typically nitrogen or argon) after each precursor pulse to remove excess precursor from the process chamber and prevent 'parasitic' CVD deposition on the substrate.

ALD had been developed and introduced worldwide with the name Atomic layer epitaxy (ALE) in the late 1970s.<sup>[2]</sup> For thin film electroluminescent (TFEL) flat-panel displays, high quality dielectric and luminescent films were required on large-area substrates, thus the deposition method of ALD was developed. Interest in ALD has increased in steps in the mid-1990s and 2000s, with the interest focused on silicon-based microelectronics. ALD is considered as one deposition method with the greatest potential for producing very thin, conformal films with control of the thickness and composition of the films possible at the atomic level. A major driving force for the recent interest is the prospective seen for ALD in scaling down microelectronic devices.

ALD can be used to deposit several types of thin films, including various oxides (e.g.  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,

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$\text{SnO}_2$ ,  $\text{ZnO}$ ,  $\text{HfO}_2$ ), metal nitrides (e.g.  $\text{TiN}$ ,  $\text{TaN}$ ,  $\text{WN}$ ,  $\text{NbN}$ ), metals (e.g.  $\text{Ru}$ ,  $\text{Ir}$ ,  $\text{Pt}$ ), and metal sulfides (e.g.  $\text{ZnS}$ ).

## ALD process

The growth of material layers by ALD consists of repeating the following characteristic four steps:

- 1) Exposure of the first precursor.
- 2) Purge or evacuation of the reaction chamber to remove the non-reacted precursors and the gaseous reaction by-products.
- 3) Exposure of the second precursor – or another treatment to activate the surface again for the reaction of the first precursor.
- 4) Purge or evacuation of the reaction chamber.

Each reaction cycle adds a given amount of material to the surface, referred to as the growth per cycle. To grow a material layer, reaction cycles are repeated as many as required for the desired film thickness. One cycle may take time from 0.5s to a few seconds and deposit between 0.1 and 3 Å of film thickness. Before starting the ALD process, the surface is stabilized to a known, controlled state, usually, by a heat treatment. Due to the self-terminating reactions, ALD is a surface-controlled process, where process parameters other than the precursors, substrate, and temperature have little or no influence. And, because of the surface control, ALD-grown films are extremely conformal and uniform in thickness.

## Advantages and limitations

### Advantages

Using ALD, Film thickness depends only on the number of reaction cycles, which makes the thickness control accurate and simple. Unlike CVD, there is less need of reactant flux homogeneity, which gives large area (large batch and easy scale-up) capability, excellent conformality and reproducibility, and simplifies the use of solid precursors. Also, the growth of different multilayer structures is straight forward. These advantages make the ALD method attractive for microelectronics for manufacturing of future generation integrated circuits. Other advantages of ALD are the wide range of film materials available, high density and low impurity level. Also, lower deposition temperature can be used in order not to affect sensitive substrates.

### Limitations

The major limitation of ALD is its slowness; usually only a fraction of a monolayer is deposited in one cycle. Fortunately, the films needed for future-generation ICs are very thin and thus the slowness of ALD is not such an important issue.

Although the selection of film materials grown by ALD is wide, many technologically important materials ( $\text{Si}$ ,  $\text{Ge}$ ,  $\text{Si}_3\text{N}_4$ , several multi-component oxides, certain metals) cannot currently be deposited by ALD in a cost-effective way.

ALD is a chemical technique and thus there is always a risk of residues being left from the precursors.

The impurity content of the films depends on the completeness of the reactions. In typical oxide processes where metal halides of alkyl compounds are used together with water as precursors, impurities found in the films are at the 0.1-1 atom % level.

## ALD in microelectronics

In microelectronics, ALD is studied as a potential technique to deposit high- $k$  (high permittivity) gate oxides, high- $k$  memory capacitor dielectrics, ferroelectrics, and metals and nitrides for electrodes and interconnects. In high- $k$  gate oxides, where the control of ultra thin films is essential, ALD is only likely to come in to wider use at the 45 nm technology. In metallizations, conformal films are required; currently it is expected that ALD will be used in mainstream production at the 65 nm node. In dynamic random access memories (DRAMs), the conformality requirements are even higher and ALD is the only method that can be used when feature sizes become smaller than 100 nm.<sup>[3]</sup>

### Gate oxides

Deposition of the high- $k$  oxides  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ , and  $\text{HfO}_2$  has been one of the most widely examined areas of ALD. The motivation for high- $k$  oxides comes from the problem of high tunneling currents through the currently used  $\text{SiO}_2$  metal-oxide-semiconductor field-effect transistor (MOSFET) gate dielectric when it is downscaled to a thickness of 1.0 nm and below. With the high- $k$  oxide, a thicker gate dielectric can be made for the required capacitance density, thus the tunneling current can be reduced through the structure.

Intel Corporation has reported using ALD to deposit high- $k$  gate dielectric for its 45 nm CMOS technology.<sup>[4]</sup>

### DRAM capacitors

The development of dynamic random access memory (DRAM) capacitor dielectrics has been similar to that of gate dielectrics:  $\text{SiO}_2$  has been widely used in the industry thus far, but it is likely to be phased out in the near future as the scale of devices are decreased. The requirements for the downscaled DRAM capacitors are good conformality and permittivity values above 200, thus the candidate materials are different from those explored for MOSFET gate dielectrics. (For example,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ , and  $\text{HfO}_2$ ) The most extensively studied candidate has been  $(\text{Ba,Sr})\text{TiO}_3$ . ALD is a very promising method, which can satisfy the high conformal requirements of DRAM applications. A permittivity of 180 was measured for  $\text{SrTiO}_3$  and 165 for  $\text{BaTiO}_3$  when films thicker than 200 nm were post-deposition annealed, but when the film thickness was decreased to 50 nm, the permittivity decreased to only 100.<sup>[5]</sup>

### Transition-metal nitrides

Transition-metal nitrides, such as TiN and TaN find potential use both as metal barriers and as gate metals. Metal barriers are used in modern Cu-based chips to avoid diffusion of Cu into the surrounding materials, such as insulators and the silicon substrate, and also, to prevent Cu contamination by elements diffusing from the insulators by surround every Cu interconnection with a layer of metal barriers. The metal barriers have strict demands: they should be pure; dense; conductive; conformal; thin; have good adhesion towards metals and insulators. The requirements concerning process technique can be fulfilled by ALD. The most studied ALD nitride is TiN which is deposited from  $\text{TiCl}_4$  and  $\text{NH}_3$ .<sup>[6]</sup>

## Metal films

Motivations of an interest in metal ALD are

- 1) Cu interconnects and W plugs, or at least Cu seed layers for Cu electrodeposition and W seeds for W CVD,
- 2) transition-metal nitrides (e.g. TiN, TaN, WN) for Cu interconnect barriers
- 3) noble metals for ferroelectric random access memory (FRAM) and DRAM capacitor electrodes
- 4) high- and low-work function metals for dual-gate MOSFETs.

## See also

- Atomic layer epitaxy
- Chemical vapor deposition
- Thin-film deposition
- High-k dielectric

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  - First use of ALD for DRAM applications [1]
  - Suppliers of high quality ALD equipment [2][3][4]
  - Journal articles discussing ALD [5][6]
  - Academic researchers specializing in ALD [7][8][9]
  - Major conferences dedicated to ALD [10]

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